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ENCAPSULATION OF COMPOUNDS BIPHENYLS INTO SBA-15: SYNTHESIS OF COMPOSITES FOR APPLICATION

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ABSTRACT

Two novel hybrid mesoporous material BVA-SBA and BEG-SBA were designed and synthesized by a process assisted by microwave. The nanoparticles were studied by UV-vis and fluorescence spectroscopy, elemental analysis, nitrogen adsorption-desorption, RMN and FTIR. The results obtained indicates the successful immobilization of BVA and BEG in the mesoporous composite. These systems present the possibility of activating the release of the organic molecules encapsulated into SBA-15, depending on the liquid medium in which the composite are suspended.

Keywords: *microwave irradiation synthesis, encapsulated, mesoporous material*.

I. INTRODUCTION

In recent years, porous materials such as mesoporous silica of different types have been employed for hosting and promote delivery of various molecules [1]. The high surface-to-volume ratio in these materials and meso-scale (2 nm < diameter < 50 nm) pores make them useful for heterogeneous catalysis, ion exchange, gas sensing and alternate energy applications [2]. In fact, the development of drug release systems based in these materials has experienced a remarkable growth and is now an important market for the industrial sector [3].

Silica-based ordered mesoporous materials is interesting because are suitable for the architecture of chemosensors [4]. In this sense, mesoporous materials are used as scaffolds for the modification of probe molecules that provide recognition and signal transduction in the detection of ions. The pores can be used to immobilize optically active probe molecules. The specific surfaces can be used to provide sites for the adsorption and diffusion of targets and enhance the local concentration [5]. Commonly, organic guests can be immobilized either on the surface or within the channels of the silicate host [6]. The using of silica SBA-15 as a coating material is based on the straight channel which facilitating the entering and diffusion of the target ions. Though SBA-15 itself is non-fluorescent, it can supply a layer of abundant hydroxyl groups as the binding sites for covalent grafting of silylation reagents [7].

In this work, the selected support for encapsulation of organic compound was SBA-15. According to development of green sustainable synthetic methods, we proposed the synthesis of SBA-15 using microwave irradiation (MW). The adoption of MW irradiation drastically reduced reaction times, increased production yields and reduced the production cost compared with conventional heating [8].

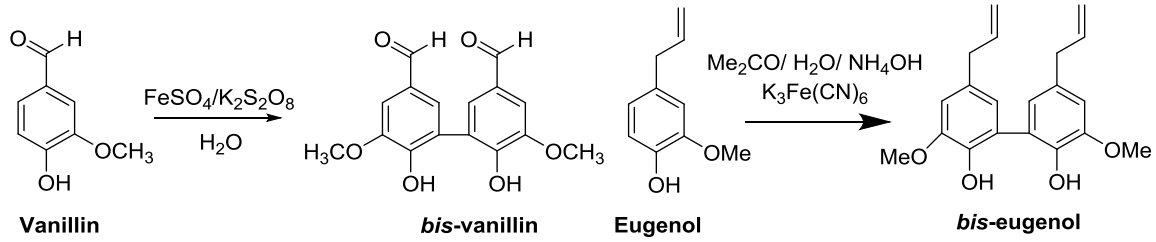
For investigating the state of compound biphenyls within the channels of hybrid material and the properties of composites, we characterize these hybrid mesoporous materials through NMR, elemental analysis (EA), nitrogen adsorption-desorption isotherms, Fourier-transform infrared spectroscopy (FTIR), UV-vis and fluorescence spectroscopy. The conditions were established to be able to evaluate the application on the synthesis of chemical sensors embedded on SBA-15 in future.

II. EXPERIMENTAL

Synthesis and preparation of materials

Bis-vanillin (BVA) was prepared with good yield (90 %), by oxidative coupling the vanillin carried out in the presence of ferrous sulfate and potassium persulfate in aqueous solution [9]. Vanillin (3.55 g, 23.33 mmol) in aqueous solution was added ferrous sulfate (0.135 g, 0.89 mmol) with vigorous stirring. Then 10 minutes,

potassium persulfate (3.38 g, 12.51 mmol) was added and the reaction mixture was maintained for 5 days at 50 °C. The solid was filtered and drying in a stove at low temperature.
Bis-eugenol (BEG) was synthesized by oxidative coupling reaction too, according to reference [10]. It consisted of the dropwise addition at room temperature of an aqueous solution of potassium ferricyanide for 5 hours, into a dilute solution of the eugenol (3 g, 18.27 mmol) in acetone (60 ml) and ammonium hydroxide 28% (40ml). More ammonium hydroxide (40 ml) was added to maintain the alkalinity in the reaction medium and the mixture stirred overnight. The reaction was neutralized with diluted hydrochloric acid and it was allowed to stand for 1 hour. The solid was filtered, washed with distilled water, dried and recrystallized with ethanol absolute (yield: 90%).
The synthetic pathway of both is depicted in Scheme 1.



Scheme 1. Synthesis route used for the preparation of compound biphenyls. a) bis-vanillin. b) bis-eugenol.

Mesoporous silica SBA-15 was carried out by using Pluronic P123 triblock copolymer as the template in acid media [11]. In a typical synthesis, 4 g of triblock P123 was dissolved in 350 ml of 3.1 M aqueous HCl solution under stirring. Then, polyetilenglicol 400 (10 g) was added and the resulting solution was slowly stirred at 35 °C until the solution became clear. Then, tetraethyl orthosilicate (TEOS, 22.5 mL) was added dropwise to the solution at room temperature. The mixture was stirred at 40 °C for 24 h. Subsequently, the container was transferred to a microwave oven and kept at 100 °C for 12 h under static conditions. The resultant precipitate was filtered, washed carefully with distilled water, and dried at 80 °C overnight. Finally, the surfactant template was removed by calcination at 550 °C for 5 h in air and to obtain the final product SBA-15.
Hybrid mesoporous material, BVA-SBA and BEG-SBA, were prepared using an Anton Paar Monowave 300. In the vial was put the corresponding biphenyl (0.15 g), SBA-15 (1.5 g) and a solution of ethanol:water (50:50, v/v) (18 mL) respecting that order. The suspension was place in MW. The conditions of reaction were: 70 ºC, 1200 rpm, 20 min. After cooling the mixture to room temperature, the product was dried at 80ºC for 5 h.

Characterization
Compound biphenyls were characterized by NMR spectra (^{1}H and ^{13}C) using a Bruker DPX-300 spectrometer.
The structure of our hybrid composites were examined by elemental analysis (EA), nitrogen adsorption-desorption isotherms, FTIR, Si-NMR, UV-vis and fluorescence spectroscopy.
Elemental analyses (C, H) were carried out in a LECO CHN628 Series Elemental Determinators. The Brunauer, Emmett and Teller (BET) method was measured by nitrogen adsorption-desorption isotherms were measured on a NOVA-1000 Quantachrome at -196 ºC. Before testing, the samples were treated at 100 ºC in the degassing port of the adsorption anaylized. Pore size distribution was calculated using the Barret-Joyner-Halenda (BJH) algorithm on the adsorption branches.
The FTIR spectra of the samples were recorded on a Shimadzu FTIR Prestige-21 spectrophotometer in the region of 4000-400 cm^{-1}. The samples were mixed with KBr (1% wt) and pressed. UV absorption spectra were performed on a Perkin Elmer Lambda 20 using quartz cells of 1.0 cm path length. Fluorescence measurements were made on a Perkin Elmer F7000 spectrophotometer with a xenon lamp as the excitation source. High-resolution solid-state ^{29}Si cross polarization/magic angle spinning (CP/MAS) spectra for SBA-15, BVA-SBA and BEG-SBA were recorded using a Bruker Avance II-300 spectrometer (59.6 MHz).

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Release test of compound biphenyls

Composites release tests were carried out by determining the amount of BVA and BEG released from powder a using different liquid mediums with a composite:medium ratio (1/100 g/mL). The liquid mediums selected for BVA-SBA were DMSO/water (1:99, v/v), DMSO, water and ethanol/water (50:50 v/v), while for BEG-SBA were acetone, acetone/water (1:99, v/v), water and ethanol/water (50:50, v/v). The amount of BVA and BEG from the powders was determinated by UV-vis spectrophotometry. The calibration curve was obtained from standard solutions of BVA (λ = 308 nm) and BEG (λ = 282 nm).

III. RESULTS AND DISCUSSION

Compound biphenyl characterization

The characterizations of compound biphenyls were:

BVA: ^{1}H NMR (DMSO-d_6, 300 MHz): 3.83 (s, 6H, OCH_3); 7.36 (d, 2H, C_{Ar}-H); 7.32 (d, 2H, C_{Ar}-H) 9.71 (s, 2H, CHO). ^{13}C NMR (DMSO-d_6, 300 MHz): 192 (CHO); 148 (C-4); 129 (C-6); 128 (C-1); 125 (C-5); 110 (C-2). IR (KBr, cm^{-1}): 3264.2 (OH); 1674.2 (C=O); 1587.4 (C=C_{Ar}).

BEG: ^{1}H RMN (Acetone-d_6, 300 MHz) d (ppm): 6,82 (s, 2H, H_{Ar}); 6,72 (s, 2H, H_{Ar}); 6,01 (m, 2H, HC); 5,11 (d, 2H, HC=C); 5,02 (d, 2H, HC=C); 3,87 (s, 6H, CH_3); 3,35 (d, 4H, CH_2). IR (KBr, cm^{-1}): 3530 (OH); 2885 (=CH); 2880 (-CH_2-); 2850 (-OCH_3); 1665 (C=C); 1620 (C=C_{Ar}); 1470 (C=C_{Ar}); 1370 (C=C_{Ar}).

Theoretical calculations were determined for the Gaussian 09 program, using DFT calculations with the gradient corrected by the Becke's parameters in combination with the correlation of Lee, Yang and Parr (B3LYP) and using 6-31G(d,p) set of base functions. The geometries of the molecules studied were optimized and the calculations of their vibration frequencies were performed to ensure the presence of a total minimum energy value. From these geometries, the values of the molecular diameter (MD) were obtained (Figure 1). The values obtained shows that the molecule of BEG (14 Å) is slightly larger than the BVA (11 Å).

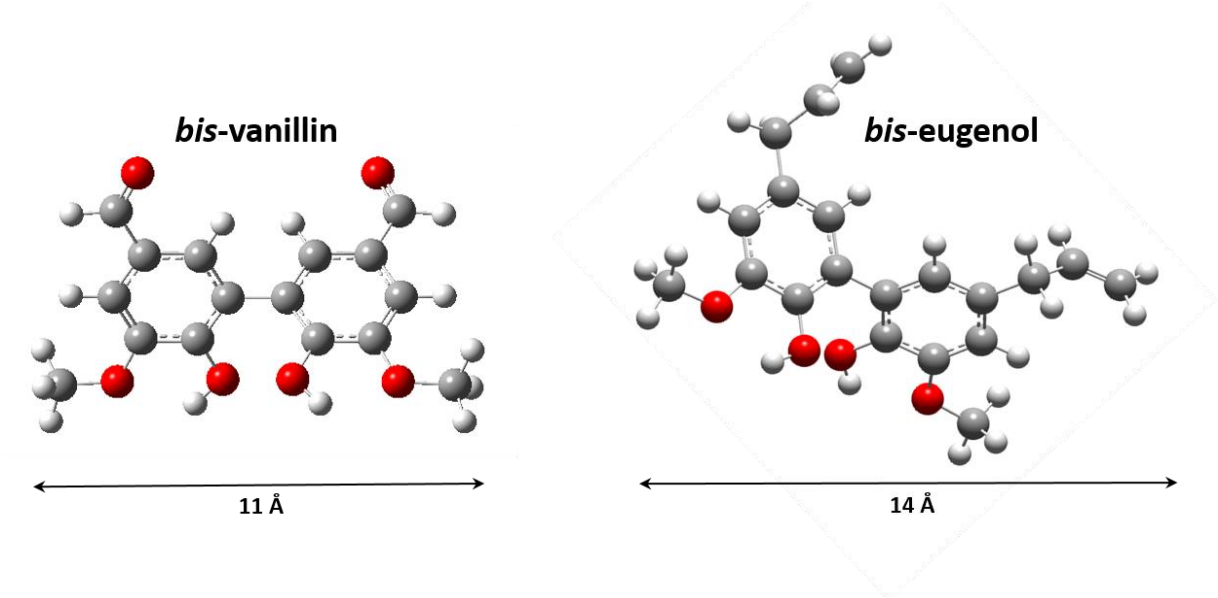

Figure 1. Optimized geometries of bis-vanillin and bis-eugenol.

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Composites characterization

Figure 2 shows the nitrogen adsorption-desorption isotherms and the pore size distribution curves of parent SBA-15, BVA-SBA and BEG-SBA. The isotherms of these mesoporous silicas are of type IV with H1 hysteresis loop at relative pressure (P/P_0) from 0.7 to 0.98 that is representative of the mesoporous cylindrical. The values of the specific surface area, pore volume and pore diameter of SBA-15 agree with those reported in the literature [12,13,14,15] and summarized in Table 1. The encapsulation of BVA and BEG into SBA-15 caused a slight increase of average pore diameter, a reduction of specific surface area and a pore volume almost unchanged. The molecular diameters of BVA and BEG calculated by DFT made possible understand that these molecules can be easily located within the pores of SBA-15. Therefore, the changes of textural parameters can be interpreted as BVA and BEG molecules within the pores of the mesoporous silica hindering the adsorption of nitrogen.

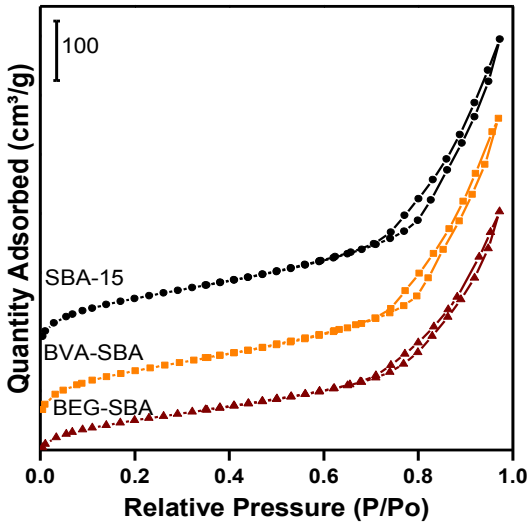

Figure 2. Nitrogen adsorption-desorption isotherms of SBA-15, BVA-SBA and BEG-SBA.

Table 1. Textural parameters of mesoporous silicas measured by N_2 adsorption-desorption isotherms

Sample	Specific Surface Area (m^2/g)	Pore Volume (cm^2/g)	Average Pore Diameter (Å)
SBA-15	420	0.77	83
BVA-SBA	387	0.78	89
BEG-SBA	264	0.61	100

FTIR spectra are reported in Figure 3 and confirm the interaction between silanol groups of mesoporous silica with molecules of BVA and BEG present into SBA-15 pores. Spectrum a corresponding to SBA-15 show a peak near 1635 cm^{-1}, mainly resulting from the bending vibration of the H_2O absorbed. The typical Si-O-Si bands appear in OH bending region as three peaks: one broad and strong peak centered at 1033 cm^{-1}; two narrow and relatively weak peaks near 805 and 463 cm^{-1}, which are associated with the condensed silica network [6,15]. The characteristic peaks in the characterization BVA and BEG were obtained from spectra b and c respectively. Encapsulation of BVA

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and BEG into SBA-15 produced the reduction of the intensity of the band at 964 cm^{-1} of silica (spectra e and c), which indicates a strong interaction between silanol groups of silica with molecules of BVA and BEG present into SBA-15 pores.

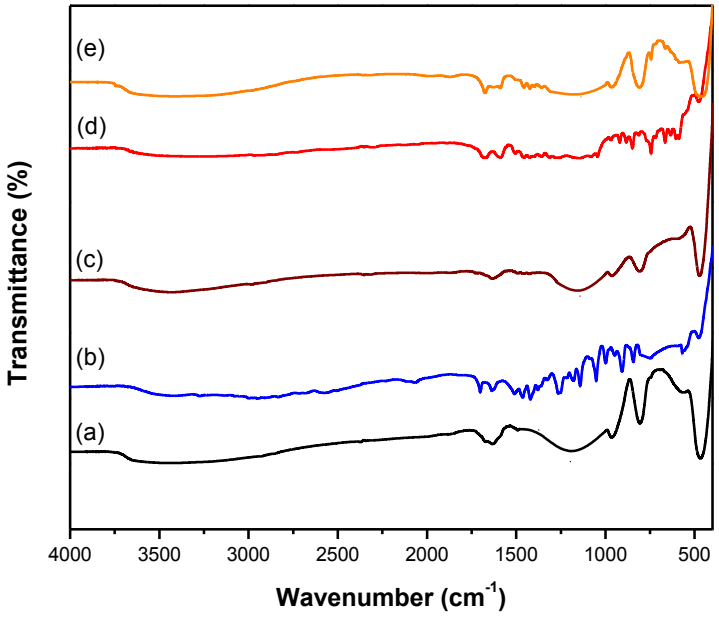

Figure 3. IR spectra of a) SBA-15, b) BEG, c) BEG-SBA, d) BVA and e) BV-SBA.

^{29}Si NMR analysis was carried out to confirm the embedding of BVA and BEG in SBA. The spectra are reported in Figure 4. The spectrum of SBA shows three resonance peaks, attributed to silicon-bond structures characterized by the absence of hydroxyl groups [$(SiO)_4Si$], the presence of isolated silanol groups [$(SiO)_3Si–OH$], and geminal silanol groups [$(SiO)_2Si–(OH)_2$], identified as Q_4 (d = -111 ppm), Q_3 (d = -103 ppm), and Q_2 (d = -93 ppm), respectively [15]. Similar spectra were obtained for composites (Figure 4, b and c). Only the proportion of peak attributed at Q_4 slightly increased as result of the interaction of precursor molecules with silanol groups of SBA-15.
To explore synthesized composites as precursors of fluorescence sensors, a study of fluorescence spectroscopy was carried out. The fluorescence spectrum of SBA-15 systems with BVA and BEG are shown in Figure 5. Mesoporous silica SBA-15 itself showed no fluorescence, whereas BVA showed an excitation band at 601 nm (λ_{EM} = 400 nm) and BEG presented an excitation band at 595 nm (λ_{EM} = 420 nm). The luminance phenomena of compound biphenyls were caused by the π electron conjugate system present in these molecules. The mesoporous hybrid materials of BVA-SBA and BEG-SBA gave a sensitive fluorescence response, at the same wavelength as the free precursors. The fluorescence appears at a definite excitation length owing to the fluorescent of BVA and BEG molecules embedded in the mesoporous silica. It can be seen, the fluorescence intensity of hybrid material of SBA decreases due to the lower amount of BVA and BEG present in the suspension in the sample. Through analyses UV-vis spectroscopy were obtained similar results.

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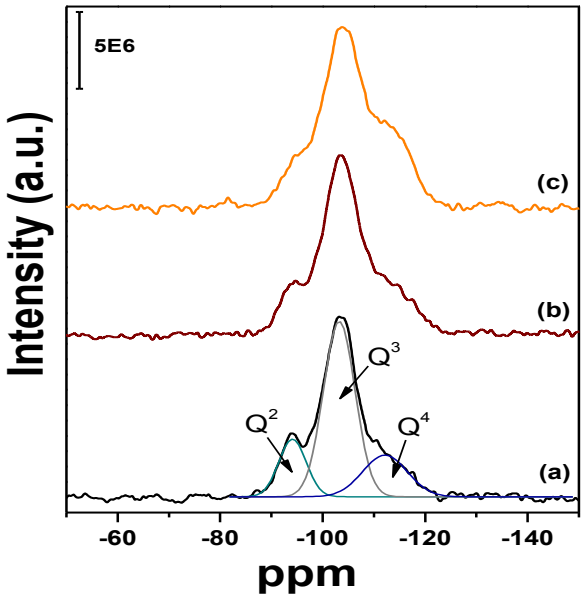
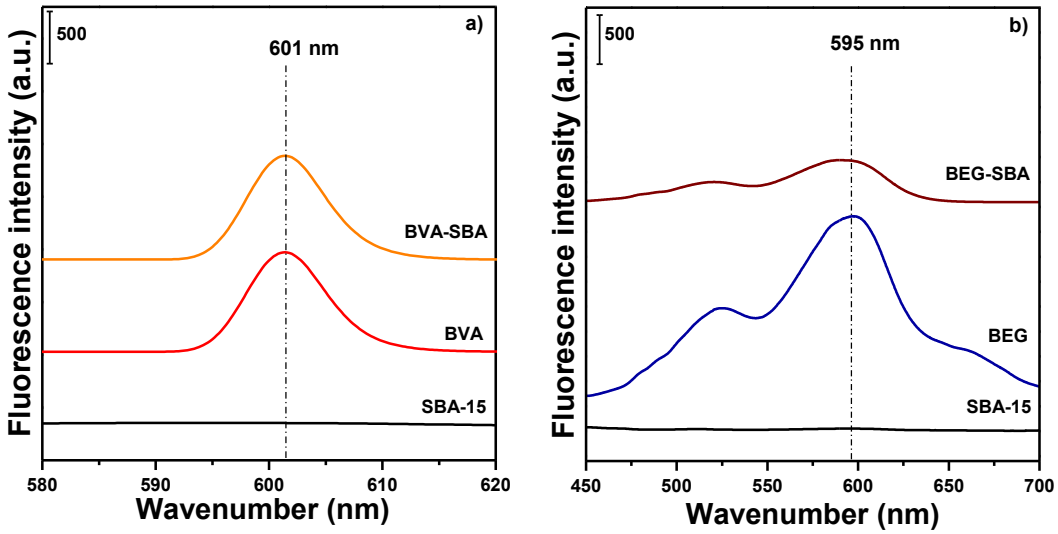


Figure 4. ^{29}Si NMR spectra of (a) SBA-15, (b) BEG-SBA and (c) BVA-SBA.



(a) (b)

Figure 5. Fluorescence spectrum of SBA-15 with: a) BVA, b) BEG.

Results shown that there are not changes in the compound of BVA and BEG encapsulated into SBA-15. It suggests weak interactions of electrostatic nature (hydrogen bond) that connect *bis*-vainillin and *bis*-eugenol with Si-OH groups present on the wall of SBA-15.

Release test

Released tests of compound biphenyls were carried out in order to investigate the effect of encapsulation of these organic molecules into SBA-15. The encapsulation of BVA and BEG could be used for different applications depending on the objective. In some cases it could be interesting that BVA and BEG remain attached to SBA-15 pores, while in others it could be attractive the release of them. As demonstrated in Table 2, results show that a medium with a high percentage of organic solvents favors the release of compound biphenyls, while the aqueous solvents do not favor their release from the SBA matrix.

The higher release of BVA and BEG from SBA in organic solvents should be attributed to the solubilization of the compound biphenyl in the solvents tested, and the easy diffusion of the molecules from the silica matrix to the medium.

Table 2. Release test of compound biphenyls in different liquid medium

Liberation of BVA (%)			**Liberation of BEG (%)**		
Liquid medium	*0.5 h*	*2.5 h*	*Liquid medium*	*0.5 h*	*2.5 h*
Water	2.67	4.85	Water	0.035	0.036
Ethanol:water	5.31	6.87	Ethanol:water	0.14	0.17
DMSO:water	15	70	Acetone:Water	1.05	20
100	50	99	Acetone	25	100

IV. CONCLUSIONS

New hybrid mesoporous materials, BVA-SBA and BEG-SBA, have been prepared via microwave-assisted process. The study of molecular diameters of BVA and BEG calculated by DFT were calculated to demonstrate the size of each one. The spectroscopic characterization and surface properties confirmed that the ordered structure of SBA-15 can be maintained after the inclusion of the BVA and BEG host molecules. These organic molecules interact weakly with the walls of SBA-15 through hydrogen bonds, producing no chemical changes in the structure of the silica. The most attractive characteristic of these systems is the possibility of activating the release of the organic molecules encapsulated into SBA-15.

V. ACKNOWLEDGEMENTS

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